

Nanostructured Sodium Molybdate Anodes for Enhanced Bioelectricity Generation and sustainable Wastewater Treatment in Microbial Fuel Cells

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Abstract: Abattoir wastewater (ABW) is characterized by extremely high organic loads, posing serious environmental and management challenges. Conventional treatment methods are often inadequate, highlighting the urgent need for advanced, sustainable technologies. Microbial fuel cells (MFCs) offer a promising dual solution by integrating wastewater treatment with renewable bioelectricity generation; however, their performance is limited by inefficient anode materials. To address this gap, this study investigates sodium molybdate dihydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) nanoparticles as a novel catalyst for anode modification in MFCs treating ABW. The nanoparticles were synthesized using sodium borohydride as a reducing agent and characterized by UV-Vis spectra, FT-IR (functional groups), XRD (size and crystal structure), and TEM (morphology), revealing non-uniform particles within 20–100 nm. MFCs performances were evaluated by comparing Na_2MoO_4 coated(doped) electrodes with unmodified graphite electrodes. Results demonstrated a significant enhancement, with the nano-coated electrode achieving a maximum voltage of 899 mV, power density of 1896 mW/m², current density of 2246 mA/m² at 3500 Ω , and 69.9% COD removal efficiency. These findings confirm that Na_2MoO_4 based nanostructured anodes can substantially improve both energy recovery and pollutant removal in MFCs, offering a sustainable approach for treating high-strength industrial effluents such as ABW.

Keywords: Abattoir wastewater (ABW); Bioelectricity Generation; Chemical Oxygen Demand (COD) removal; Nanostructured anodes; Sodium Molybdate Nanoparticles.

1. Introduction

Wastewater treatment and sustainable energy generation are pressing global concerns, particularly given the depletion of fossil fuels and rising environmental pollution [1,2]. Conventional wastewater treatment methods are often energy-intensive and insufficient for the removal of complex and emerging contaminants, highlighting the need for alternative, eco-friendly technologies [3,4]. Microbial fuel cells (MFCs) have gained attention as a dual-function system capable of simultaneously



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treating wastewater and generating renewable bioelectricity. In MFCs, electroactive bacteria oxidize organic matter at the anode, releasing electrons that travel through an external circuit to the cathode, where they react with oxygen and protons to form water [5,6]. This process directly converts the chemical energy of organic substrates into electricity via microbial metabolism, offering a sustainable solution for energy recovery and wastewater remediation [7,8].

Abattoir wastewater (ABW) represents one of the most challenging effluents due to its complex composition of proteins, fats, carbohydrates, nitrogen, and phosphorus, as well as extremely high biochemical oxygen demand (BOD) and chemical oxygen demand (COD) [9–13]. Its high organic load not only poses environmental hazards but also provides a rich substrate for microbial bioelectrochemical conversion, making ABW a promising candidate for MFC-based treatment and energy generation [14–15]. However, MFC performance is often constrained by electrode limitations, particularly at the anode, where efficient electron transfer and biofilm formation are critical. Losses associated with bacterial electron transfer, internal resistance, and cathodic reactions reduce overall system efficiency [16,17]. Recent advances in nanotechnology provide opportunities to overcome these limitations. Nanomaterials such as nanowires, nanotubes, and nanoparticles exhibit unique physical, chemical, and electrical properties, including high surface area, improved conductivity, and enhanced microbial adhesion, which can significantly boost MFC output [17]. Nanoparticles of metal oxide have shown potential in improving anode conductivity, reducing resistance, and enhancing bioelectricity generation [18,19]. In this context, the present study investigates sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) nanoparticles as a novel nano catalyst for anode modification in MFCs treating abattoir wastewater. The synthesized nanoparticles were characterized and their influence on power generation and COD removal efficiency systematically evaluated.

2. Research and Methodology

2.1. Materials (Heading two)

Sodium molybdate dihydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$), sodium borohydride (NaBH_4) potassium dihydrogen phosphate, disodium hydrogen phosphate, hydrogen chloride, and sodium hydroxide were bought from a store. All chemicals used for synthesis and electrode preparation were typically of analytical grade and used without purification. The water used for the experiment was distilled water and it was used throughout the experiments. Plastic containers were used as MFCs chamber, glass wares, cable wires, and cylindrical graphite rod electrodes were used for this study.

Abattoir wastewater (ABW) was collected from a wastewater reservoir at an abattoir located along Ogbomoso–Ilorin Road, Oyo State, Nigeria ($08^\circ 10' \text{N}$, $04^\circ 10' \text{E}$) [20]. The samples were obtained in clean 25 L plastic containers with airtight covers, transported to the laboratory, and stored under anaerobic conditions. To allow sedimentation of suspended solids, the wastewater was left undisturbed for 24 h at room temperature (25°C). A portion of the supernatant was then taken for physicochemical characterization following standard methods [21].

2.2. Experiments

2.2.1. Construction and Preparation of MFC

A dual-chamber microbial fuel cell (MFC) was fabricated locally using two identical plastic containers fitted with airtight covers, following the design reported by [22]. The anode chamber was supplied with abattoir wastewater (ABW) as the substrate, while the cathode chamber contained a phosphate buffer solution. Two types of electrodes were employed; an unmodified graphite electrode (control) and a graphite electrode coated with sodium molybdate nanoparticles to enhance electrical conductivity and facilitate efficient electron transfer. The cathode chamber was maintained at pH 7.5,

whereas the anode chamber was operated under its initial environmental conditions COD and BOD (722.74 and 4226.4 mg/l)

2.2.2. Nanomaterial Preparation

Sodium molybdate nanoparticles were synthesized via a hydrothermal method following [23]. Two grams of sodium molybdate dihydrate were dissolved in 100 mL of distilled water under continuous stirring at room temperature. A freshly prepared 0.05 M ice-cold sodium borohydride (NaBH_4) solution [24] was added dropwise to the precursor solution (pH adjusted to 7.5) while stirring, keeping the reaction temperature below 10°C to control reactivity [25]. The mixture was then gradually heated to $30\text{--}40^\circ\text{C}$, during which the color changed from colorless to deep brown, indicating nanoparticle formation. Stirring continued for 1–2 h to ensure completion. The product was centrifuged, thoroughly washed with ethanol and distilled water, then dried overnight in an oven at 70°C . The dried material was ground into a fine powder using a mortar and pestle, followed by calcination at 550°C to eliminate residual impurities. Finally, the sample was subjected to physicochemical characterization.

2.2.3. Preparation of Polyvinyl Alcohol (PVA) Solution

A 5.0 g portion of analytical-grade polyvinyl alcohol (PVA) powder was gradually added to 100 mL of distilled water in a conical flask under continuous stirring. The mixture was heated on a magnetic hot plate at $80\text{--}90^\circ\text{C}$ for 40–45 min to facilitate dissolution. Heating continued until a clear, homogeneous, and viscous solution was obtained, confirming complete solubilization. The solution was then cooled naturally to room temperature (25°C) and stored for subsequent electrode coating, following [26].

2.2.4. Preparation of MoO–PVA Composite for Electrode Coating

Sodium molybdate nanoparticles (0.5 g) were dispersed in ethanol and probe-sonicated for 15–30 min. The required concentration (1–5 wt% relative to PVA) was incorporated into the cooled PVA solution under stirring, followed by 15 min of sonication. Graphite electrodes were pretreated and sonicated in water bath with ethanol for 30 min, then oven-dried at $50\text{--}55^\circ\text{C}$. The MoO–PVA composite was drop-cast onto the electrode surface and dried sequentially in air and oven ($50\text{--}60^\circ\text{C}$, 2–3 h). Coated electrodes were stored in a desiccator for subsequent use in microbial fuel cells [27].

2.3. Products Characterization

2.3.1. Physico-chemical analysis of ABW

The ABW sample was analyzed for physicochemical parameters including biological oxygen demand (BOD), chemical oxygen demand (COD), pH, total dissolved solids (TDS), total suspended solids (TSS), and selected heavy metals (zinc and lead). All analyses were performed according to the Standard Methods for the Examination of Water and Wastewater APHA, [28]. At the point of collection, preliminary parameters such as color, odor, pH, dissolved oxygen (DO), and electrical conductivity (EC) were recorded. pH was determined using a digital pH analyzer (HQ40d, HACH, USA), while EC was measured with a portable conductivity meter (HACH, USA). DO concentration was measured with a portable DO meter (HI 9143, HANNA, Italy).

2.3.2. Characterization of molybdate nanoparticles

The visual properties of molybdate nanoparticles were able to analyze using a UV–Vis double-beam spectrophotometer (Agilent Cary 60 UV/Vis) with 1-cm path length Hellma quartz cuvettes range from 200–800 nm. The samples were examined using X-ray diffraction (XRD) for crystalline structure, TEM analysis was conducted and operating at 200 KV. Samples of nanoparticle were dispersed

ultrasonically in ethanol, then placed on a carbon coated copper grid and the image showed quasi-spherical. Fourier-transform infrared spectra were noted using a SHIMADZU FTIR-8000 spectrometer in the range of 4000 to 400 cm^{-1} , with samples prepared in powdery form.

2.3.3. Measurement and Analysis

The voltage (mV) generated through the microbial fuel cell was systematically measured using a digital multimeter with an autorange function. Current generated and power outputs were calculated using Ohm's law formula. Water quality parameters including electrical conductivity, total dissolved solids (TDS) and pH, were measured using a multiparameter analyzer (HANNA Probe). Chemical oxygen demand (COD) removal efficiency, wastewater samples were collected and analyzed using closed reflux method with potassium dichromate as the oxidizing agent, following spectrophotometric analysis with a Spectroquant (Merck) system, following the procedure described in [29]. Resistance is calculated according to Ohms law using eq.1:

$$V = IR \quad (1)$$

Where V is voltage, I is current, and R is resistance. The projected area of electrode of graphite electrode was calculated for power area density as shown in eq.2, the area power density was calculated using equation 3: where P_{AD} is the area of power density Wm^{-2} .

$$P_{AD} = \frac{I \times V}{A} \quad (2)$$

2.3.4. Chemical Oxygen Demand (COD) Determination

The chemical oxygen demand (COD) of the wastewater samples was determined to estimate the total oxygen required for the oxidation of organic matter in the presence of a strong oxidizing agent. The procedure followed the Standard Methods for the Examination of Water and Wastewater (APHA, [28]). A digestion solution was prepared using potassium dichromate (0.1 M) in sulfuric acid containing silver sulfate as a catalyst. Ferrous ammonium sulfate (FAS) was employed as the titrant, with ferroin indicator for end-point detection. Wastewater samples and blanks were digested in COD vials using a COD reactor at elevated temperature of 2 h. After cooling, the digested samples were diluted with distilled water and titrated against FAS. COD values were calculated by subtracting the blank from the titration volume of the samples and expressed in mg/L of O_2 . The COD measurement was calculated in eq. 3 below and the COD reduction efficiency in eq.4.

$$COD_{mg/l} = \frac{(Blank - Sample) \times Normality \text{ of FAS} \times Dilution \text{ Factor} \times 8000}{Amount \text{ of Sample taken}} \quad (3)$$

calculated by using equation 4 below, where: COD_E is COD efficiency removal, COD_{in} is COD initial and COD_{out} is COD Final

$$COD_E (mg/l) = \frac{COD_{in} - COD_{out}}{COD_{in}} \times 100\%$$

3. Results and Discussion

3.1. Physico-chemical properties

Physicochemical properties of ABW were analyzed to assess the quality of water sample and suitability for microbial fuel cell (MFC) applications. The parameters measured from ABW were as follows: total dissolved solids (TDS) : 603 mg/L; total suspended solids (TSS) : 769 mg/L; biological oxygen demand (BOD) – 4226.4 mg/L; chemical oxygen demand (COD) : 7227 mg/L; lead :3.063

mg/L; zinc : 2.855 mg/L, electrical conductivity :850 μ S/cm; and dissolved oxygen (DO) :1.62 mg/L as summarized in Table 1.

Table 1. Physico-chemical properties of ABW

Parameters	ABW	FEPA ^a	WHO ^b	USEPA ^c
pH	7.6	5.5-9.0	6.0-9.5	6.5-8.5
Color (TCU)	Black	NS	Dark Brown	-
Odor	Intolerable	NS	NS	-
TDS (mg/l)	603	2000	600	500
TSS (mg/l)	769	100	250	-
COD (mg/l)	722.74	250	-	-
BOD (mg/l)	4226.4	30	-	-
DO (mg/l)	1.62	-	-	-
Lead	3.063	-	-	65
Zinc	2.855	-	-	120
Electrical Conductivity (μ S/cm)	822	-	-	NS

*Values are means of 3 replicates, NS: Not stated; (a)[30]; (b) [31]; (c) [32] *

The physicochemical analysis of ABW revealed values far exceeding regulatory limits. TSS (769 mg/L) and COD (722.74 mg/L) surpassed FEPA (100 mg/L) and USEPA (250 mg/L) thresholds, while BOD (4226.4 mg/L) was alarmingly higher than the FEPA guideline of 30 mg/L, confirming a heavy organic load. The very low DO (1.62 mg/L) indicates severe oxygen depletion, consistent with the black color and intolerable odor, from abattoir effluents. Although pH (7.6) was within acceptable limits, TDS (603 mg/L) approached WHO limits (600 mg/L), and trace metals such as Pb (3.063 mg/L) and Zn (2.855 mg/L) also raised concern, posing toxicity risks if discharged untreated. Such extremely organic and solid loads highlight the need for advanced treatment. Microbial fuel cells (MFCs) are particularly suited as they not only reduce COD and BOD but also generate bioelectricity through microbial metabolism, turning pollution into a resource [33, 34]. The high biodegradable fraction in ABW provides a rich substrate for exoelectrogenic bacteria, making MFCs a promising eco-friendly approach for both energy recovery and wastewater remediation

3.2. Chemical Characterization of Nanomaterial

3.2.1. UV-Vis Spectroscopy Analysis

The UV–Vis absorption spectrum of sodium molybdate nanoparticles (Na_2MoO_4 -NPs) exhibited a distinct peak at approximately 280 nm, which corresponds to charge transfer transitions from oxygen to molybdenum ions. The sharp and symmetrical nature of this peak suggests successful nanoparticle formation with narrow size distribution and good crystalline, characteristics that are highly desirable for electrochemical applications [35]. In the context of Microbial Fuel Cells (MFCs), such well-structured nanoparticles play a crucial role in enhancing performance. The strong absorption in the UV region indicates efficient electron transition properties, which can directly improve electron shuttling and catalytic activity at the electrode–microbe interface. This facilitates faster redox reactions, improving power density and coulombic efficiency during wastewater treatment. Compared to broader absorption peaks often reported for molybdate nanoparticles synthesized via conventional routes [36], the sharp 280 nm peak observed in this study highlights the superior optical and electronic properties of the Na_2MoO_4 -NPs produced. These properties are expected to reduce charge transfer resistance, thereby enhancing COD/BOD removal efficiency and overall MFC sustainability. Thus, the

UV–Vis result not only confirms nanoparticle formation but also underscores their potential to synergistically improve wastewater treatment efficiency while recovering energy in MFC systems [37].

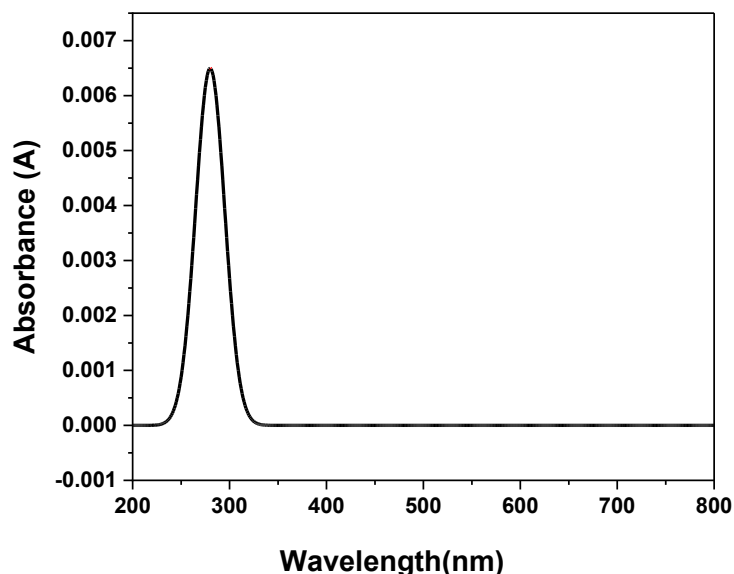


Figure 1. UV-Vis Spectrophotometer shows the wavelength versus absorbance of Na_2MoO_4 -NPs

3.2.2. Fourier Transmission Infrared (FTIR) Spectroscopy Analysis

FTIR spectrum analysis was employed to know the bonding structure and functional groups of Na_2MoO_4 -NP synthesized via chemical using NaBH_4 as shown in Figure 2. FTIR analysis of Na_2MoO_4 -NPs showed bands at ~ 845 , 791 , and 736 cm^{-1} corresponding to $\text{Mo}=\text{O}$ terminal and $\text{Mo}-\text{O}-\text{Mo}$ bridging vibrations, matching reports of $\text{O}-\text{Mo}$ stretching in molybdate literature [38,39]. The UV-Vis absorption at $\sim 280\text{ nm}$ confirms the MoO_4^{2-} charge transfer transitions [40], collectively validating the structural integrity of the synthesized nanoparticles. These results align with the UV–Vis absorption peak at 280 nm , confirming successful formation of stable sodium molybdate nanoparticles suitable for MFC electrode application

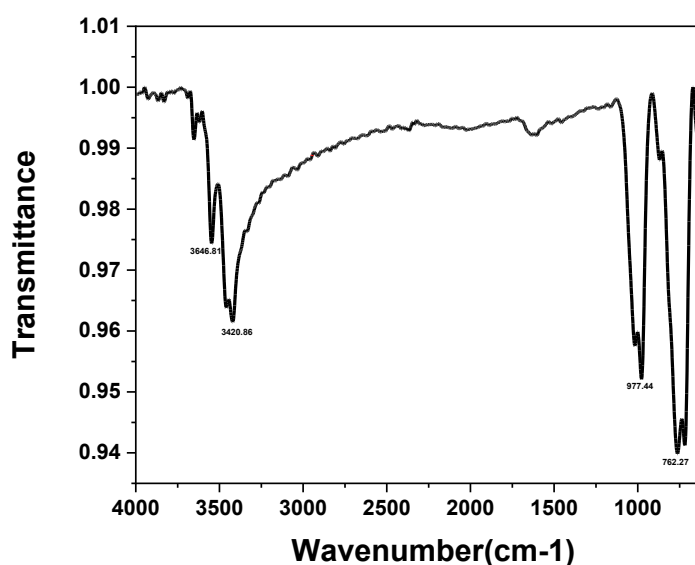


Figure 2. FT-IR spectra of Na_2MoO_4 -NPs

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3.2.3. X- Ray Diffraction (XRD) Analysis of Na₂MoO₄

Crystalline structure of the synthesized sodium molybdate (Na₂MoO₄) nanoparticles from NaBH₄ was analyzed using X-ray diffraction (XRD) as shown in Figure 3. XRD pattern of this synthesized Na₂MoO₄ nanoparticles mostly shows prominent diffraction peaks at 2 (θ) which is approximately 13.2°, 23.4°, 27.3°, 33.1°, 38.49°, 39.3°, 50.2°, 58.8°, 66.5°, and 78.3° values. These peaks nearly match the orthorhombic phase of molybdenum trioxide (α -MoO₃) which was compared to JCPDS database file No. 05-0508. From Figure 3. The XRD analysis shows a strong peak at 38.49 and 44.73 degrees, and this corresponds to the 83.33 plane, signifying high crystallinity in the direction. This match shows the presence of MoO₃ well crystallized in the sample solution. It showed partial oxidation of molybdate while synthesis or during drying. Also, the broadening peak showed nanoscale particle dimensions which was due to the nanoscale crystallite size and strain effects as described in [41]. Moreso, the molybdenum trioxide nanoparticles were estimated by Debye-Scherrer equation as shown in eq. 5. Where d is average crystallite size, k-Scherrer constant (0.89), λ - X ray wavelength (0.14nm) and β is the full width at half maximum intensity of the peak at the diffracting angle θ

$$d = \frac{K\lambda}{\beta \cos \theta} \quad (5)$$

From the eq.5, the average crystallite size of molybdenum oxide nanoparticles was calculated to be 33.6 nm. The size of the nanoparticles agreed with the result reported by [42] for sodium molybdate synthesized via chemical, showing successful nanostructure formation from sodium borohydride.

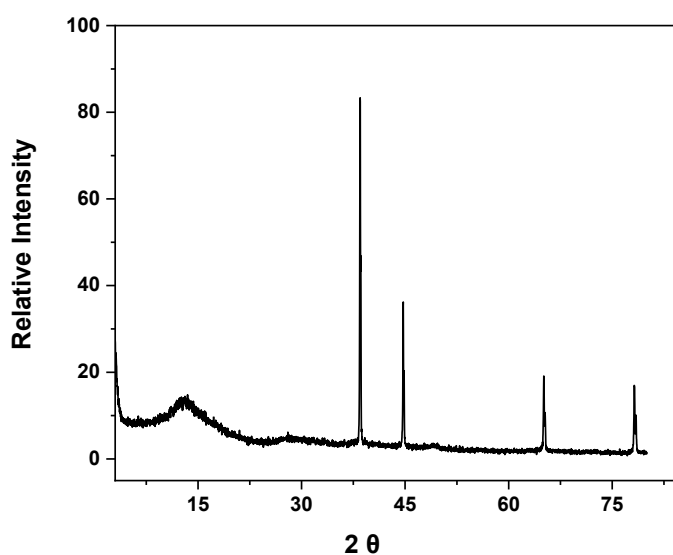


Figure 3. XRD pattern of prepared NaMoO₄

3.2.3. Transmission Electron Microscopy (TEM) Analysis

TEM images as shown in Figure 4 revealed sodium molybdate nanoparticles (Na₂MoO₄-NPs) with sizes ranging from ~1.3 to 5.3 nm, displaying predominantly spherical to quasi-spherical morphology with moderate agglomeration. The nanoscale size confirms the stability of the synthesized nanoparticles even after exposure to the complex wastewater matrix, the particles retained their structural integrity, demonstrating resistance to dissolution or significant aggregation during treatment [43,44]. The persistence of such small particle sizes is highly beneficial for **microbial fuel cell (MFC) applications**, as the enhanced surface area facilitates stronger microbial adhesion and more efficient

electron transfer at the electrode interface. This directly contributes to improved power generation and accelerated biodegradation of organic pollutants. Moreover, the catalytic activity of molybdate-based nanomaterials supports redox reactions, further enhancing **chemical oxygen demand (COD) reduction** during treatment. Thus, the TEM results not only confirm the successful synthesis of Na_2MoO_4 -NPs but also validate their structural stability and functional role in enhancing both **electricity** generation and wastewater purification efficiency [45, 46]

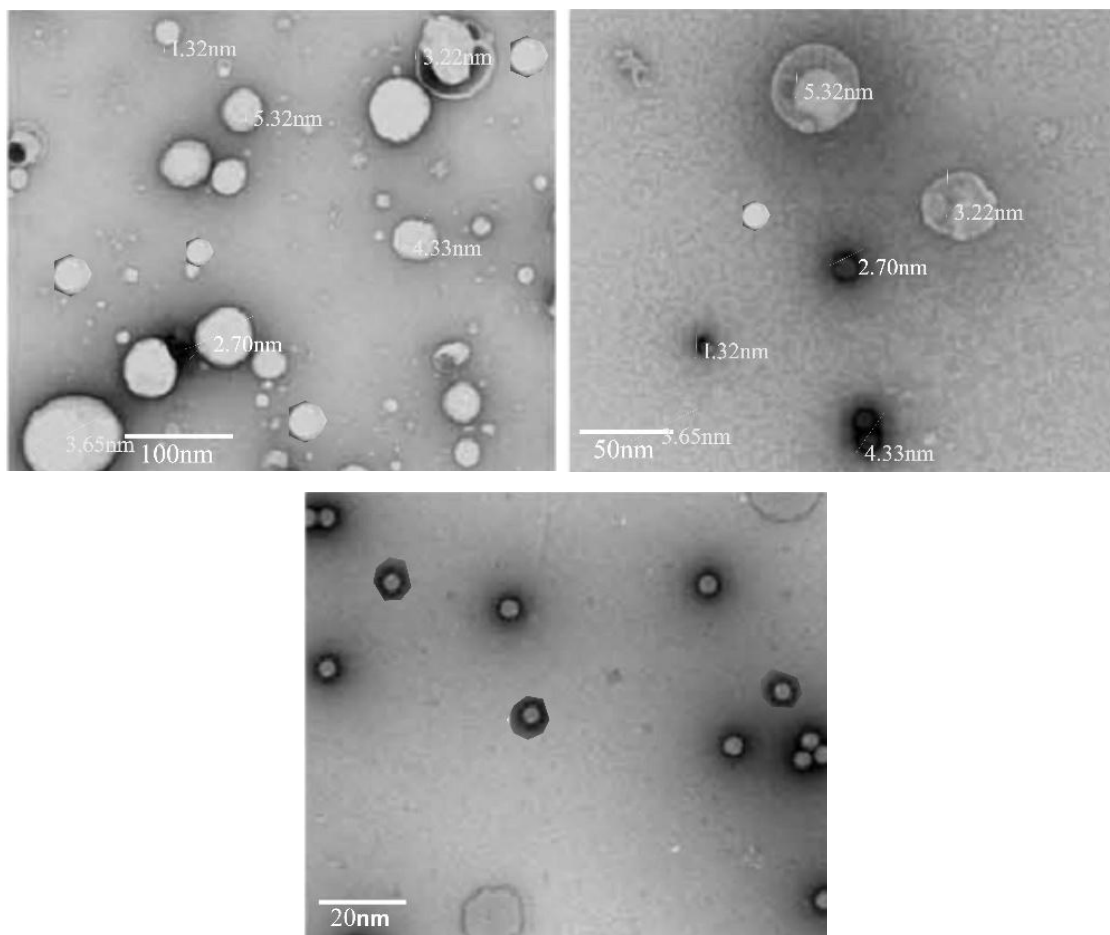


Figure 4. Transform Electron Microscope (TEM) shows wastewater reduction.

3.2.4. Bioelectricity Generation

Figure 5 compares the voltage profiles of abattoir wastewater (ABW) using a plain electrode (control/unmodified) and a sodium molybdate nanoparticle (Na_2MoO_4 -NP) doped (modified) electrode. The results clearly show that nanoparticle incorporation significantly enhanced microbial activity, leading to more stable and higher voltage generation. With the plain electrode, the maximum voltage obtained was 412 mV after 10 days, whereas the nanoparticle-modified electrode achieved a much higher peak voltage of 899 mV after 11 days. This improvement can be attributed to the catalytic role of Na_2MoO_4 -NPs, which facilitate efficient electron transfer and create a more favorable environment for microbial adhesion and biofilm formation on the electrode surface. The observed trend indicates that bioelectricity generation initially increased, reached a peak, and then gradually declined toward the end of the cycle, reflecting the dynamics of microbial growth and substrate utilization. These findings are consistent with previous reports where nanomaterial-modified electrodes improved electron transfer efficiency and stabilized MFC performance (47,48).

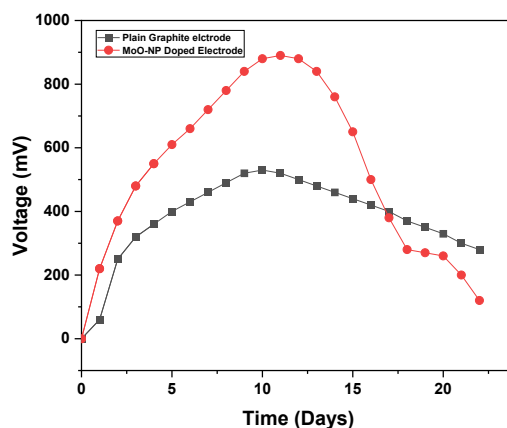


Figure 5. Voltage generated (mV) as a function of time under OCV for plain graphite electrode and MoO₄-NP

3.4. Polarization curve and power density of MFC

The performance of the microbial fuel cell (MFC) was assessed using polarization and power density curves. Voltage and current values were measured under varying external resistances (100 Ω –10 k Ω), and power density was calculated to evaluate electrical output relative to the substrate volume. As shown in Figure 6a and 6b, the coated electrode system significantly outperformed the plain (control) electrode. At higher external resistances, the voltage dropped, indicating that the bacterial community could not adapt efficiently to the increased electron flow rate. This trend aligns with previous studies, where current density decreased with rising resistance due to electron transfer limitations [49, 50, 51]. The Na₂MoO₄ nanoparticle-coated electrode achieved a maximum power density of 1896 mW/m² with a corresponding current density of 2246 mA/m² at 3500 Ω . In contrast, the plain electrode reached only 665.34 mW/m² at 1525 mA/m² under the same conditions. These results highlight the role of nanoparticle modification in enhancing electrochemical performance by improving electron transfer and microbial-electrode interactions. The findings are consistent with recent reports that nanomaterial-coated electrodes significantly improve MFC power output while simultaneously aiding wastewater treatment [52,53]. Furthermore, COD removal efficiency reached 69.9%, demonstrating the dual benefit of enhanced electricity generation and effective pollutant removal.

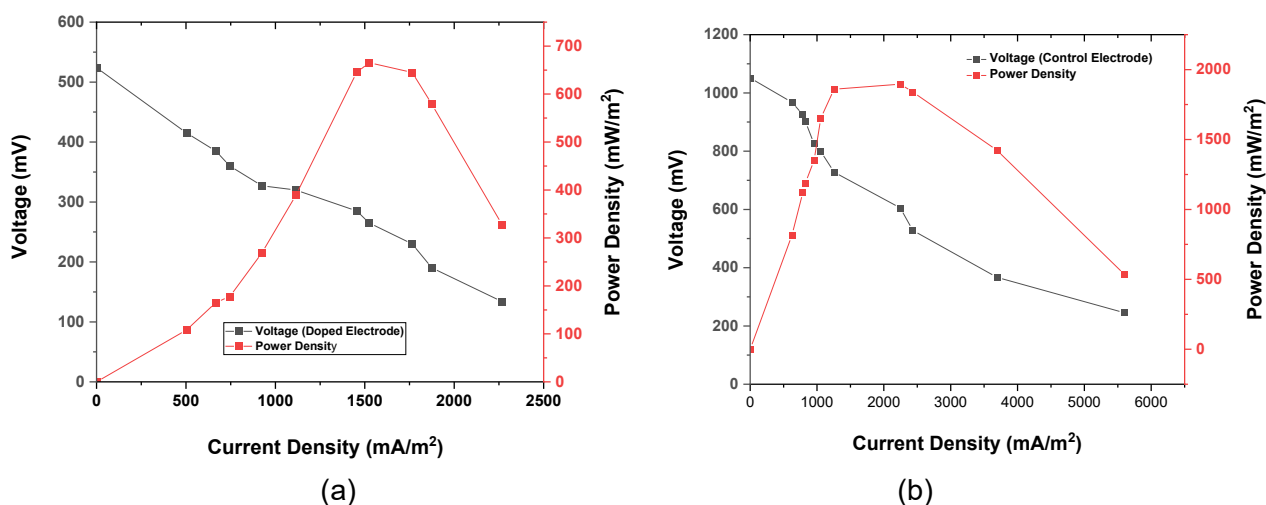


Figure 6. Polarization curves depicting bioelectricity generation and power density performance of (a) NaMoO₄ doped electrode and (b) control electrode

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4. Conclusion

A novel sodium molybdate (Na_2MoO_4) doped graphite anode was successfully developed to enhance electricity generation in microbial fuel cells (MFCs). TEM analysis confirmed the structural integrity of the nanoparticles, while electrochemical testing demonstrated superior performance of the coated electrode, achieving a peak voltage of 899 mV compared to 412 mV with uncoated control. The low cost, simple preparation, and high efficiency of Na_2MoO_4 make it a promising electrocatalyst for MFCs. Overall, sodium molybdate nanoparticles improved wastewater treatment efficiency, enhanced electron transfer, promoted biofilm development, and significantly increased power output, underscoring their potential for sustainable bioenergy applications.

Author contributions: Conception and design of the study were done by Agarry Samuel and Odunayo Akinwumi. Material preparations were done by Fajobi Oluwateniola, Oloyede Victoria and Abioye Oyindamola, Methodology was designed by Akinwumi Odunayo and Aremu Mujidat, Analysis was carried out by Akinwumi Odunayo, data collection and analysis were done by all authors. Original manuscript was written by Akinwumi Odunayo and all authors commented on the manuscript. All authors read and approved the final manuscript.

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Conflict of Interest: The authors declare that there is no conflict of interest regarding the publication of this paper.

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